A Conservative Evaluation of the Transport of TCE from the Confined Aquifer beneath J-Field, Aberdeen Proving Ground, Maryland, to a Hypothetical Receptor

A Conservative Evaluation of the Transport of TCE from the Confined Aquifer beneath J-Field, Aberdeen Proving Ground, Maryland, to a Hypothetical Receptor

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Foreword

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Notation

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this document. Some acronyms used in tables or equations are defined only in the respective tables or equations.

Acronyms, Initialisms, and Abbreviations

APG	Aberdeen Proving Ground
DCE	dichloroethene
DNAPL	dense nonaqueous-phase liquid
MSL	mean sea level
TBP	Toxic Burning Pits
TCE	trichloroethylene
VC	vinyl chloride
VOC	volatile organic compound

Units of Measure

d	day(s)	L	liter(s)
ft	foot (feet)	lb	pound(s)
ft^3	cubic foot (feet)	m	meter(s)
g	gram(s)	µg	microgram(s)
gpm	gallon(s) per minute	mi	mile(s)
kg	kilogram(s)	mL	milliliter(s)
km	kilometer(s)	ppb	part(s) per billion
		ppm	part(s) per million

Abstract

Past disposal operations at the Toxic Burn Pits (TBP) area of J-Field, Aberdeen Proving Ground, Maryland, have resulted in volatile organic compound (VOC) contamination of groundwater. Although the contaminant concentration is highest in the surficial aquifer, VOCs are also present in the confined aquifer, which is approximately 30 m (100 ft) deep at the TBP area. This study focuses on the confined aquifer, a sandy valley-fill Pleistocene unit in a paleochannel cut into Cretaceous sands and clays. This report documents the locations of the region's pumping wells, which are over 6 km (4 mi) away from the TBP. The distances to the pumping wells and the complex stratigraphy limit the likelihood of any contamination reaching a receptor well. Nonetheless, a worst-case scenario was evaluated with a model designed to simulate the transport of trichloroethylene (TCE), the main chemical of concern, from the confined aquifer beneath the TBP along a hypothetical, direct flowpath to a receptor well. The model was designed to be highly conservative (i.e., based on assumptions that promote the transport of contaminants). In addition to the direct flowpath assumption, the model uses the lowest literature value for the biodegradation rate of TCE, a low degree of sorption, a continuous-strength source, and a high flow velocity. Results from this conservative evaluation indicate that the simulated contaminant plume extends into areas offshore from J-Field, but decays before reaching a receptor well. The 5-ppb contour, for example, travels approximately 5 km (3 mi) before stagnating. Recent field analyses have documented that complete biodegradation of TCE to ethene and ethane is occurring directly below the TBP; therefore, the likelihood of TCE or its daughter products reaching a pumping well appears negligible. Thus, the model results may be useful in proposing either a no action or a natural attenuation alternative for the confined aquifer.

Section 1
Introduction

Decades of waste disposal operations have resulted in groundwater contamination at J-Field, Aberdeen Proving Ground (APG), Harford County, Maryland. Although most of the contamination is present in the surficial aquifer, the deeper, confined aquifer also has detectable levels of trichloroethylene (TCE, or TRCLE, or trichloroethene) and other volatile organic compounds (VOCs). The State of Maryland requested an evaluation of the potential risk of these contaminants to residents relying on well water in the region, which prompted this Argonne National Laboratory (ANL) study. The nearest wells are over 6 km (4 mi) from the Toxic Burning Pits (TBP). These wells are located across the Gunpowder River and Chesapeake Bay (Figure 1). That concentrations at that distance should be negligible seems obvious; however, ANL evaluated the validity of this assumption with groundwater flow and contaminant transport modeling.

The purpose of this modeling effort was to create a one-dimensional flow and transport model for analyzing the potential of contaminant transport from the confined aquifer beneath J-Field to the nearest receptor well. The model was purposefully designed to be highly conservative (i.e., to promote the transport of contaminants). Modeling results will be useful in determining whether natural attenuation or no action are reasonable alternatives for the confined aquifer.
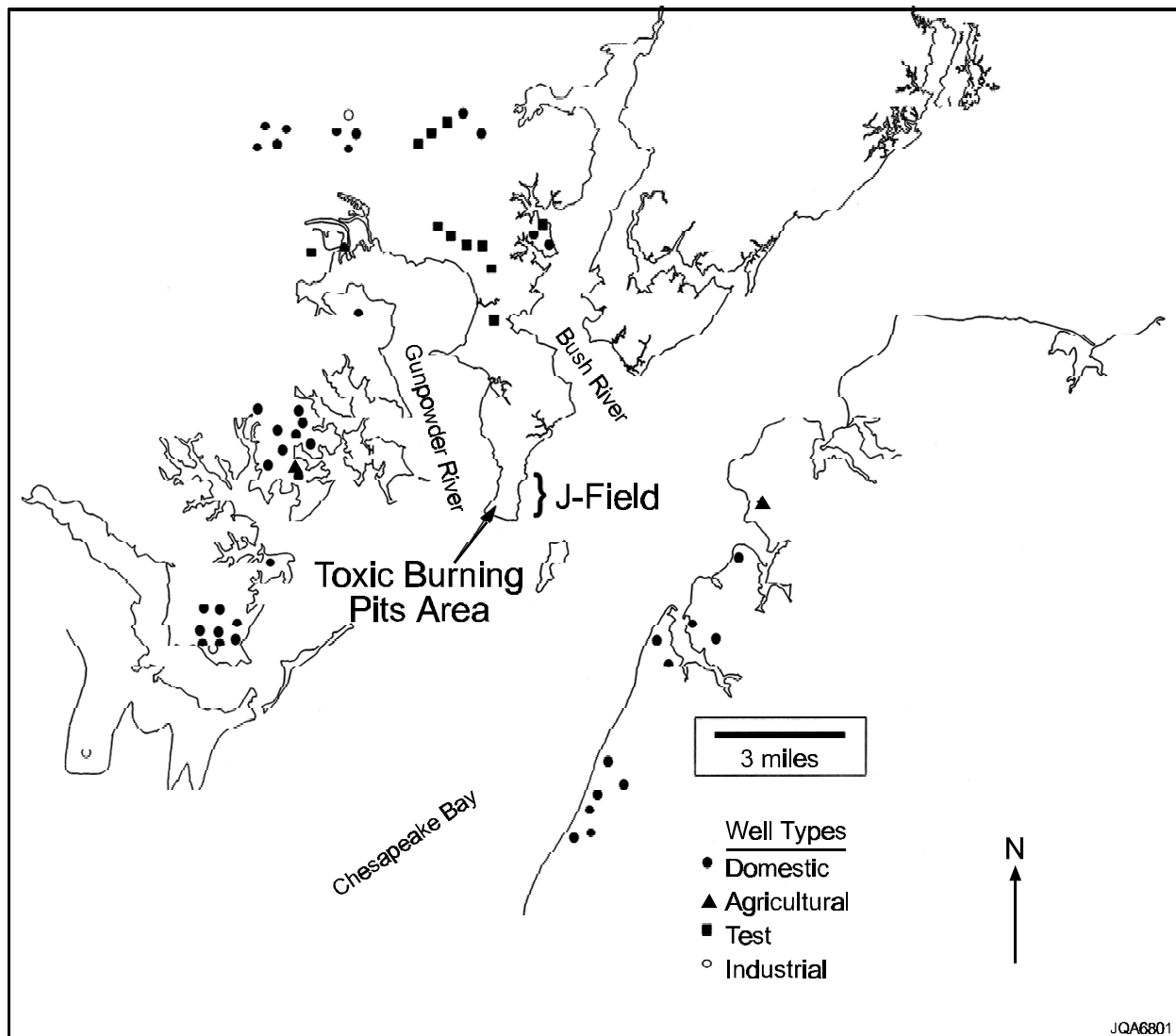
Figure 1 Locations of J-Field and Pumping Wells in the Region

Section 2
Site Description

2.1 Local and Regional Hydrogeology

The Chesapeake Bay region is underlain by Cretaceous deposits of the Patapsco
Formation of the Potomac Group. These sediments form a complex framework of sandy
aquifers and massive clay units (Hughes 1993). The coastal Cretaceous deposits were
subjected to fluctuating sea levels during the Pleistocene. This resulted in complex
erosional and depositional environments, including three main systems of paleochannels
cut into the Cretaceous units by the ancient Susquehanna River (Colman et al. 1990).
These paleochannels, identified regionally by marine geophysics and drilling records, are
present at different depths. Typically, each paleochannel contains infill units of a basal
sand and gravel, which grade into the clay and silt of an estuarine deposit. On a regional
scale, the stratigraphy is only generally understood from a limited number of boreholes
and geophysical surveys. What is known is that a great deal of complexity is present in
both the Pleistocene and Cretaceous deposits. Regional cross sections produced by the
U.S. Army Corps of Engineers (COE 1997) illustrate the highly variable nature of
permeable and impermeable units in the subsurface of the APG region.

The confined aquifer at J-Field is the deepest of three main Pleistocene units of the
Talbot Formation that fill a paleochannel (Hughes 1993). The other units are a surficial
silty sand aquifer and an intervening fine-grained confining unit. The confined aquifer
beneath J-Field is composed of highly permeable sand and gravel at an approximate depth
of 30 m (100 ft) (Hughes 1993). The thickness of this unit in the TBP area ranges from 4
to 15 m (13 to 50 ft) (Hughes 1993); its thickness is likely to vary greatly with distance
from J-Field. In the immediate vicinity of J-Field, the paleochannel has a northwest to
southeast trend. The Cretaceous formations containing the paleochannel deposits include
a complex assemblage of sandy and clayey units (Hughes 1993; COE 1997).

Flow in the confined aquifer had been thought to be radial from the J-Field peninsula
under low horizontal hydraulic gradients (Hughes 1993). Because of diurnal tidal loading
in the confined aquifer (see Hughes 1993, Figure 31), hand measurements of water levels
of confined aquifer wells are of limited use. Therefore, continuous recorder data from
seven confined aquifer wells at J-Field from the 1993 water year were analyzed to provide
a more accurate picture of the overall head distribution (Quinn et al. 1996). The results
confirm radial flow (Figure 2). The greatest average horizontal hydraulic gradient
indicated by these heads is 3.4×10^{-4} between wells JF61 and JF41. The gradients
decrease closer to the shore.

Where the paleochannel extends beneath the Chesapeake Bay, groundwater probably
discharges upward to the bay (Hughes 1993; Powars 1997). The rate of discharge is most
likely minimal because of the low hydraulic conductivity of the overlying confining unit
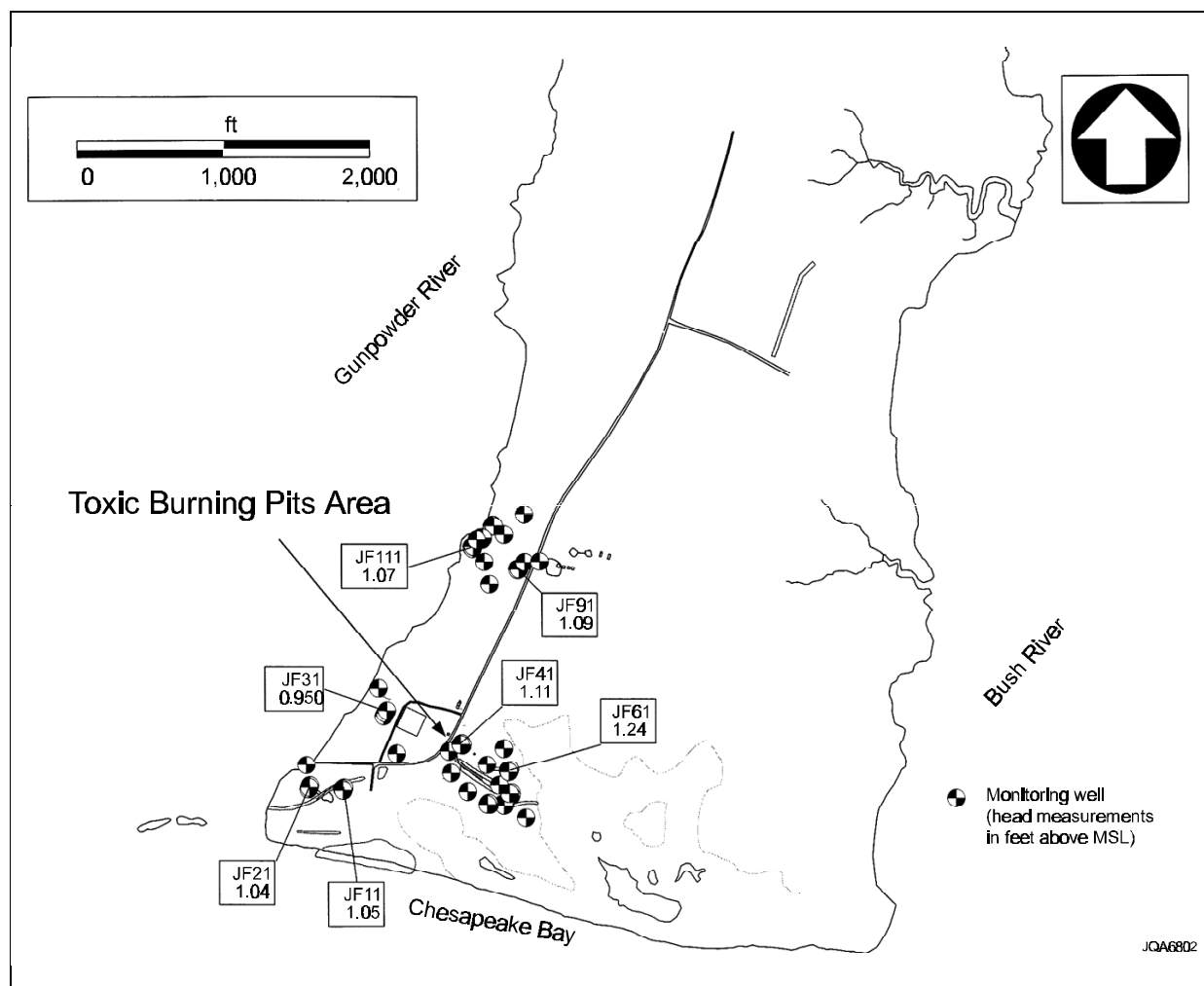
Figure 2 Locations of the Toxic Burning Pits Area and Mean 1993 Head Measurements in the Confined Aquifer

and the low vertical head gradient across the confining unit (Hughes 1993). The degree of connection between the confined aquifer and any permeable portions of the Cretaceous units along the paleochannel wall has not been established.

Because the timing and magnitude of the tidal loading effect are independent of position relative to the J-Field shore, it is assumed to have no impact on lateral groundwater flow within the confined aquifer.

In the deeper Cretaceous sediments, most of the regional flow from the portions of Maryland on the western and eastern shores of the bay discharges slowly to the bay (Otton and Mandle 1984). Flow within the Cretaceous units is primarily in poorly connected sand bodies, and the connections between these sands are not clearly understood because of considerable spatial variation (Otton and Mandle 1984). Even at

the scale of site-specific investigations, the Cretaceous sand/clay architecture is difficult to decipher (Hughes 1993; Tenbus and Fleck 1996).

Slug tests performed on four monitoring wells in the confined aquifer at J-Field provided a range of hydraulic conductivity values from 1.1×10^{-3} to 3.2×10^{-1} (3 to 900 ft/d) (Hughes 1993). The lower values at two wells represented a portion of the aquifer with a relatively high silt and clay content; values from the other two wells represent sand zones.

Drummond and Blomquist (1993) compiled hydraulic conductivity information on Cretaceous coastal plain aquifers in Harford County. A range from 2.1×10^{-3} to 3.1×10^{-1} (6 to 870 ft/d) is presented, with a median of 3.0×10^{-1} (85 ft/d).

2.2 Regional Pumping Stresses

To evaluate possible regional influences of pumping wells on the confined aquifer beneath J-Field, a survey of wells within a 13.7-km (8.5-mi) radius of J-Field (measured from the southern tip of Rickett's Point Road) was conducted. Because of the depth of the confined aquifer at J-Field, shallow wells (those less than approximately 27 m [90 ft] deep) were ignored in the survey, since they are not likely to have a strong connection to the deeper groundwater flow system. Locations of deep wells in the survey are shown in Figure 1.

Well applications processed since 1969 for designated areas and well completion reports were obtained from the Groundwater Permits Program, Maryland Department of Environment, Baltimore, Maryland. General information pertaining to production at well fields was obtained from Drummond and Blomquist (1993).

The wells were placed into three groups on the basis of their location relative to J-Field. To the north, the major pumping centers are associated with the towns of Edgewood and Joppatowne and primarily service domestic and small commercial users (Table 1). The largest pumping center in Harford County is the well field at Perryman, 11 km (7 mi) to the northeast of Edgewood, which produced an average of 11.7 million L/d (3.1 million gal/d) in 1989 from the Potomac Group sediments. The town of Aberdeen produced an average of 4.9 million L/d (1.3 million gal/d) from two well fields in 1989. Pumping at the Edgewood Area of APG was negligible in 1989.

The pumping centers to the west and southwest of J-Field service primarily domestic, agricultural, and small commercial users (Table 2). Most of these wells were completed at depths less than 27 m (90 ft), with a range from 4 to 208 m (14 to 684 ft); six wells (3 domestic, 2 industrial, and 1 agricultural) are greater than 52 m (170 ft). The largest pumping center is Bethlehem Steel Corp., 19 km (12 mi) to the west-southwest, which draws from the deeper Potomac Group sediments (at a depth of 208 m [684 ft]) and has a capacity of about 4.5 million L/d (1.2 million gal/d).

Table 1 Deep Wells to the North of J-Field

No.	Well ID	Depth/Screen[a] (unit, description)[a]	Distance from J-Field (to nearest half mile)	Type (capacity)
1	GA-72-0166	113 ft	6.5 mi N-NE	Domestic (15 gpm, test)
2	HA-81-3019	145 ft	6.5 mi N-NE	Test (1 gpm, test) U.S. Army
3[b]	HA-81-3020	170 ft/160–165 ft (Patapsco, sand and gravel under clay)	6.5 mi N-NE	Test (1 gpm, test) U.S. Army
4	HA-81-1166	107 ft	6.5 mi N-NE	Domestic (20 gpm, test)
5	HA-81-1616	88 ft	4.5 mi N	Test (1 gpm, test) Commander, APG
6	HA-81-2989	145 ft	6.5 mi N-NW	Test (1 gpm, test) U.S. Army
7	HA-81-2990	180 ft	6.5 mi N-NW	Test (1 gpm, test) U.S. Army
8	HA-81-4078	95 ft	6.0 mi N-NW	Test (1 gpm, test) U.S. Army
9	HA-81-2997	99 ft	6.0 mi N-NW	Test (1 gpm, test) U.S. Army
10	HA-81-3005	90 ft	6.0 mi N-NW	Test (1 gpm, test) U.S. Army
11	HA-81-3006	107 ft	6.0 mi N-NW	Test (1 gpm, test) U.S. Army
12	HA-81-1494	139 ft	5.5 mi N	Test (1 gpm, test) U.S. Army
13	HA-81-4167	140 ft	8.0 m N-NW	Test (50 gpm, test) Harford Co. DPW
14	HA-81-4166	157 ft	8.0 N-NW	Test (162 gpm, test) Harford Co. DPW

Continued

Table 1 Deep Wells to the North of J-Field (Cont.)

No.	Well ID	Depth/Screen[a] (unit, description)[a]	Distance from J-Field (to nearest half mile)	Type (capacity)
15	HA-81-4130	150 ft	8.5 mi N-NW	Test (15 gpm, test) Maryland Geological Survey
16	GA-73-0774	130 ft	8.5 mi N	Domestic (10 gpm, test)
17	GA-73-1260	138 ft	8.5 mi N	Domestic (10 gpm, test)
18	HA-81-2452	125 ft	8.5 mi N-NE	Domestic (20 gpm, test)
19	BA-81-4948	100 ft	7.5 mi N-NW	Test (1 gpm, test) Enviro-Gro Tech
20	HA-73-5234	100 ft	7.5 mi N-NW	Domestic (7 gpm, test)
21	BA-81-4357	150 ft	9.5 mi N-NW	Domestic (15 gpm, test)
22	BA-88-2088	300 ft	9.0 mi N-NW	Domestic (no data)
23	BA-73-6603	127 ft	9.5 mi N-NW	Domestic (12 gpm, test)
24	HA-70-0399	100 ft	9.5 mi N-NW	Domestic (3 gpm, test)
25	HA-72-0355	170 ft	9.5 mi N-NW	Domestic (15 gpm, test)
26	HA-73-0239	236 ft	9.5 mi N-NW	Domestic (4 gpm, test)
27	HA-73-5109	150 ft	9.5 mi N-NW	Domestic (2 gpm, test)
28	HA-73-5341	275 ft	9.5 mi N-NW	Domestic (12 gpm, test)
29	HA-73-5446	325 ft	9.5 mi N-NW	Domestic (2 gpm, test)
30	HA-73-5865	300 ft	9.5 mi N-NW	Domestic (6 gpm, test)
31	HA-73-5950	250 ft	9.5 mi N-NW	Domestic (7 gpm, test)
32	HA-81-1465	250 ft	9.5 mi N-NW	Domestic (12 gpm, test)
33	BA-92-0930	200 ft	9.5 mi N-NW	Domestic (5 gpm, test)
34	HA-70-0352	355 ft	9.5 mi N-NW	Domestic (6 gpm, test)

Continued

Table 1 Deep Wells to the North of J-Field (Cont.)

No.	Well ID	Depth/Screen[a] (unit, description)[a]	Distance from J-Field (to nearest half mile)	Type (capacity)
35	HA-71-0497	142 ft	9.5 mi N-NW	Domestic (30 gpm, test)
36	HA-72-0418	290 ft	9.5 mi N-NW	Domestic (50 gpm, test)
37	HA-73-0610	207 ft	9.5 mi N-NW	Domestic (5 gpm, test)
38	HA-73-1764	250 ft	9.5 mi N-NW	Domestic (20 gpm, test)
39[b]	HA-73-1774	375 ft/100–375 ft (Patapsco, hard grey rock)	9.5 mi N-NW	Domestic (30 gpm, test)
40	HA-73-2060	275 ft	9.5 mi N-NW	Domestic (6 gpm, test)
41	HA-73-2123	150 ft	9.5 mi N-NW	Domestic (15 gpm, test)
42[b]	HA-73-4585	350 ft/85–350 ft (Patapsco, black rock)	9.5 mi N-NW	Industrial (2 gpm, test)
43	HA-73-4789	105 ft	9.5 mi N-NW	Domestic (7 gpm, test)
44	HA-81-1002	135 ft	9.0 mi N-NW	Domestic (7 gpm, test)
45	HA-81-2373	200 ft	9.0 mi N-NW	Domestic (7 gpm, test)
46	BA-81-2872	90 ft	5.5 mi N-NW	Domestic (30 gpm, test)

[a] If available.

[b] Well completion reports obtained for these wells include a well log and the results of a pumping test.

To the east and southeast, across Chesapeake Bay, the pumping centers service primarily domestic and agricultural users (Table 3). Most of these wells were completed at depths less than 27 m (90 ft), with a range from 4 to 60 m (24 ft to 196 ft); two domestic wells are greater than 58 m (190 ft) deep. The average daily quantities needed for these wells are generally less than 3,800 L/d (1,000 gal/d); the application record for one agricultural well reports a capacity of 270,000 L/d (72,000 gal/d).

Pumping stresses have a negligible effect on the confined aquifer at J-Field because of the distances involved and the complex stratigraphy. Even at the Graces Quarters portion of APG, located northwest of J-Field across the Gunpowder River, the influence of unknown off-site pumping wells on a confined Cretaceous aquifer is minimal (Tenbus and Fleck 1996).

Table 2 Deep Wells to the West and Southwest of J-Field

No.	Well ID	Depth/Screen[a] (unit, description)[a]	Distance from J-Field (to nearest half mile)	Type (capacity)
1[b]	BA-81-3199	225 ft/215–225 ft (Patapsco, fine sand under sand and white clay)	5.5 mi W-SW	Domestic (7 gpm, test) ADQN[c] = 1,000 gal/d
2[b]	BA-81-2741	684 ft/640–684 ft (Patapsco, green clay and rock under coarse white sand and mixed clays)	12.0 mi W-SW	Industrial (800 gpm, test) Bethlehem Steel Corp.
3	BA-81-5684	110 ft	6.0 mi W-NW	Domestic (7 gpm, test)
4	BA-73-6521	100 ft	6.0 mi W-NW	Domestic (5 gpm, test)
5	BA-81-0550	130 ft	5.5 mi W-NW	Domestic (7 gpm, test)
6	BA-88-0164	125 ft	5.5 mi W-NW	Domestic (7 gpm, test)
7[b]	BA-92-0595	173 ft/166–173 ft (Patapsco, sand under red clay)	5.0 mi W-NW	Domestic (7 gpm, test)
8	BA-73-2658	130 ft	5.0 mi W-NW	Domestic (7 gpm, test)
9	BA-81-5445	140 ft	5.0 mi W-NW	Domestic (7 gpm, test)
10	BA-93-0154	139 ft	5.0 mi W-NW	Domestic (7 gpm, test)
11	BA-73-7197	135 ft	5.5 mi W-NW	Domestic (7 gpm, test)
12	BA-88-0946	100 ft	5.5 mi W-NW	Domestic (7 gpm, test)
13[b]	BA-81-1897	250 ft/240–250 ft (Patapsco, sand and clay under white clay)	5.0 mi W-NW	Farm (100 gpm, test)
14	BA-73-6219	145 ft	5.0 mi W-NW	Domestic (25 gpm, test)
15	BA-81-8538	110 ft	7.5 mi W-SW	Domestic (7 gpm, test)
16	BA-73-1758	100 ft	7.5 mi W-SW	Domestic (25 gpm, test)
17[b]	BA-71-0115	223 ft/218–223 ft (Patapsco, coarse sand under white clay)	7.5 mi W-SW	Industrial (5 gpm, test) Recreation and Parks
18	BA-72-0638	125 ft	7.5 mi W-SW	Domestic (40 gpm, test)
19	BA-73-0359	125 ft	7.5 mi W-SW	Domestic (20 gpm, test)
20	BA-73-6256	107 ft	7.5 mi W-SW	Industrial (20 gpm, test) Baltimore Co.

Continued

Table 2 Deep Wells to the West and Southwest of J-Field (Cont.)

No.	Well ID	Depth/Screen[a] (unit, description)[a]	Distance from J-Field (to nearest half mile)	Type (capacity)
21[b]	BA-81-3783	205 ft/195–205 ft (Patapsco, sand under sand and white clay)	7.0 mi W-SW	Domestic (12 gpm, test)
22	BA-81-1172	130 ft	7.5 mi W-SW	Domestic (50 gpm, test)
23	BA-81-1262	110 ft	7.5 mi W-SW	Industrial (45 gpm, test) Baltimore Co.
24	BA-81-5817	120 ft	7.0 mi W-SW	Domestic (7 gpm, test)
25	BA-81-3468	107 ft	7.0 mi W-SW	Domestic (40 gpm, test)
26	BA-81-0734	125 ft	7.0 mi W-SW	Domestic (7 gpm, test)

[a] If available.

[b] Well completion reports obtained for these wells include a well log and the results of a pumping test.

[c] ADQN = average daily quantity needed.

2.3 Site Contaminant Data

TCE and other VOCs have been detected in confined aquifer wells JF51, JF61, JF71, and JF81 (Table 4 and Figure 3), although an inspection of the well construction and stratigraphy presented in Hughes (1993) indicates that only well JF81 is screened in the permeable confined aquifer sediments. The TCE concentrations range from 1.8 to 1,600 ppb in these wells. The TCE regulatory limit in drinking water is 5 ppb according to Maryland Code of Regulations 26.04.01.07.

When concentrations of chlorinated solvents dissolved in groundwater exceed 1% of their solubility, the presence of a dense nonaqueous-phase liquid (DNAPL) is suggested (Remediation Technologies Development Forum 1996). Because the solubility of TCE is about 1,100 ppm, the maximum detected is only 0.15% of the solubility, which suggests that pure DNAPL is not present in the samples collected.

Table 3 Deep Wells to the East and Southeast of J-Field

No.	Well ID	Depth/Screen[a] (Unit, Description)[a]	Distance from J-Field (to nearest half mile)	Type (Capacity)
1[b]	KE-81-0515	103 ft/93–103 ft (Patapsco, dark brown sand under green sand and shells)	6.0 mi E-SE	Domestic (10 gpm, test) ADQN[c] = 300 gal/day
2	KE-81-0166	97 ft	5.5 mi E-SE	Domestic (20 gpm, test)
3	KE-81-0575	90 ft	5.0 mi E-SE	Domestic (30 gpm, test)
4	KE-73-0752	196 ft	6.0 mi E-SE	Domestic (40 gpm, test)
5	KE-81-0394	190 ft	6.0 mi E-SE	Farm (50 gpm, test) Andelot Farms
6[b]	KE-73-0120	92 ft /84–92 ft (Talbot, fine to medium grey clay)	6.5 mi S-SE	Domestic (10 gpm, test) ADQN = 1,000 gal/day
7	KE-81-0232	105 ft	6.5 mi S-SE	Domestic (30 gpm, test)
8	KE-81-1255	100 ft	7.0 mi S-SE	Domestic (15 gpm, test)
9[b]	KE-81-1470	114 ft/104–114 ft (Patapsco, white fine to coarse sand? under grey clay)	7.0 mi S-SE	Domestic (60 gpm, test)
10	KE-81-0402	95 ft	6.5 mi S-SE	Domestic (15 gpm, test)
11	KE-81-1001	93 ft	6.0 mi S-SE	Domestic (100 gpm, test)
12	KE-81-0731	88 ft	6.0 mi E-SE	Domestic (35 gpm, test)

[a] If available.
[b] Well completion reports obtained for these wells include a well log and the results of a pumping test.
[c] ADQN = average daily quantity needed.

Table 4 TCE Concentrations in Deep Wells of the Toxic Burning Pits Area

	Well			
	JF51	JF61	JF71	JF81
	Hydrogeologic Unit			
Hydrogeologic Unit	**Primarily Confining Unit**	**Primarily Confining Unit**	**Primarily Confining Unit**	**Confined Aquifer**
1990 TCE samples (ppb)	520	1.8	7.3	230
1992 TCE samples (ppb)	97	10	3	220
1994 TCE samples (ppb)	850	6	ND[a]	1,600

[a] ND = not detected.

Source: unpublished Argonne National Laboratory data.
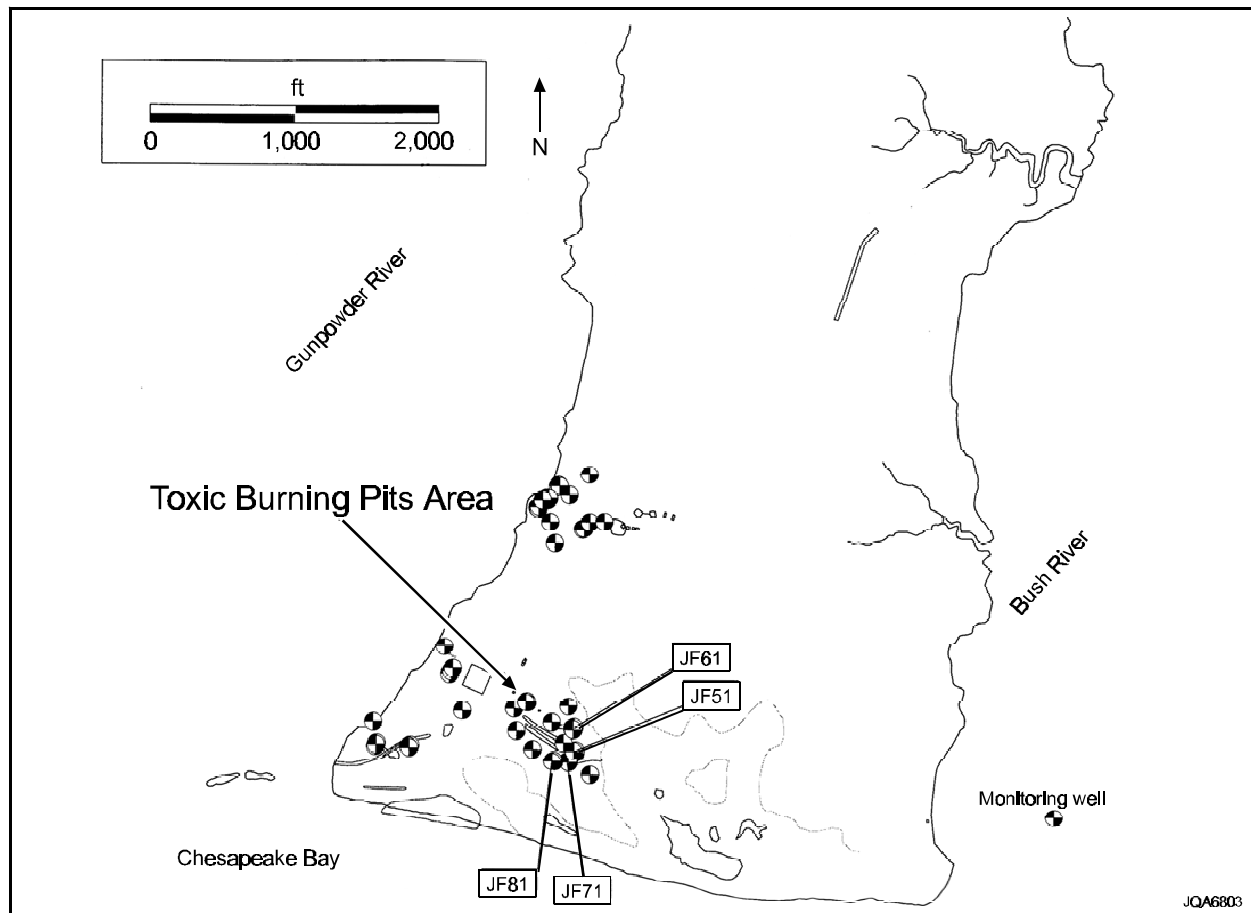

Figure 3 Locations of Deep Wells at the Toxic Burning Pits Area

Section 3
Transport of TCE in Groundwater

3.1 Contaminant Fate and Transport Processes

The rate of contaminant transport in groundwater is governed by many factors, including advection, dispersion, diffusion, dilution, retardation, and decay. Advection is the movement of dissolved contaminants along with the bulk groundwater flow. During advection, molecules spread both along and perpendicular to the flow direction, a process called dispersion. Diffusion of contaminants is typically a very slow process that occurs along a concentration gradient. The combination of advection, dispersion, and diffusion results in dilution of the contaminant.

Retardation is a slowing of the transport of contaminants relative to the bulk groundwater flow rate as the result of sorption of the contaminants onto aquifer matrix material. Sorption depends on the type of contaminant, the aquifer mineralogy, and the presence of organic matter in the aquifer matrix. Sorption of contaminants is normally described with a distribution coefficient, K_d, as shown in the following equation:

$$K_d = C_s / C_{aq}, \qquad [1]$$

where:

K_d = distribution coefficient (length/mass [L^3/M]);

C_s = mass of solute sorbed per dry unit weight of solid (M/M); and

C_{aq} = concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid (M/L^3).

The K_d is determined on the basis of the partition coefficient of the chemical with respect to organic carbon by the following relationship:

$$K_d = (K_{oc})(f_{oc}), \qquad [2]$$

where:

K_{oc} = partition coefficient with respect to organic carbon (L^3/M); and

f_{oc} = organic carbon fraction of the aquifer (unitless).

The value of K_{oc} for TCE normally ranges from approximately 40 to 200 mL/g (Fetter 1993; Mackay et al. 1993). Pankow and Cherry (1996) provide examples of

f_{oc} values, ranging from 0.0001 to 0.0075, in various sandy aquifers. Zheng and Bennett (1995) provide a range of f_{oc} values in glaciofluvial sands from 0.00017 to 0.00102.

Below a critical value for f_{oc}, the organic chemical is sorbed primarily onto the aquifer's mineral matter, rather than onto its organic matter. When f_{oc} is below this critical value, the K_d value may be underestimated by the above equation, as sorption to mineral surfaces begins to dominate. For TCE, Fetter (1993) proposed a critical f_{oc} value of 0.0007.

The K_d value affects the retardation, R, of the contaminant by the relationship

$$R = 1 + (K_d)(B_d)/n,$$
[3]

where:

R = retardation (unitless);

B_d = bulk density (M/L^3); and

n = porosity (unitless).

Retardation, R, is the ratio of the rate of bulk groundwater flow to the rate of contaminant transport. Pankow and Cherry (1996) describe TCE retardation factors at several sandy aquifers in North America. Values are generally less than 10 and usually between 1 and 2.5.

The use of K_d values is a simplifying approach to a complex process. A limitation of the method is that, by using a linear isotherm, the model does not limit the amount of solute that can be sorbed (Fetter 1993).

The decay due to biodegradation of a VOC such as TCE can be modeled in an approximate fashion by using a half-life approach. In this manner, a first-order rate of degradation of the compound due to biochemical processes governs the amount of parent chemical mass remaining.

TCE biodegrades in the aquifer environment, but its rate of natural degradation depends on subsurface conditions, including the type and prevalence of microbial populations, and whether aerobic or anaerobic conditions are present. TCE degrades to cis-1,2-dichloroethylene, with lesser amounts of trans-1,2-dichloroethylene and 1,1-dichloroethylene in an anaerobic environment (Barbee 1994). The isomers of dichloroethene (DCE) further degrade to vinyl chloride (VC). VC is commonly believed to degrade to ethene only under aerobic conditions; however, this process has also been known to occur under anaerobic conditions in a laboratory (DiStefano et al. 1991; deBruin et al. 1992; Wu et al. 1995). The ethene is further degraded to ethane (deBruin et al. 1992). Complete degradation from TCE to ethene and ethane has also been observed in the field (Cox et al. 1995; Lee et al. 1995).

Co-metabolism is the conversion of a chlorinated compound to another chemical by microorganisms during growth on other carbon compounds. In an aerobic environment, TCE can be co-metabolized along with methane, alkenes, aromatic compounds, or ammonia (Remediation Technologies Development Forum 1996). In an anaerobic situation, TCE can be co-metabolized under conditions of denitrification, sulfate reduction, and methanogenesis (Remediation Technologies Development Forum 1996).

Degradation of TCE depends on site-specific factors, including redox conditions, and decay may not follow a simple first-order model. Limited literature on the half-life estimated for TCE indicates a wide range of half-life values. Howard et al. (1991) estimated that the half-life of TCE in groundwater ranges from 10.7 months, on the basis of hydrolysis, to 4.5 years on the basis of anaerobic sediments. In the Netherlands, Zoeteman et al. (1981) estimated a half-life of 2.0 years in groundwater. Yeh and Kastenberg (1991) estimated 86 days. Cohen and Mercer (1993) provided a range of half-lives in groundwater from 321 to 1,653 days. Barbee (1994) estimated a half-life of 33 to 230 days for anaerobic degradation. A compilation of seven field-scale case studies of TCE half-lives by Wiedemeier et al. (1996) shows a range of values from 0.3 to 4.2 years.

3.2 Available Codes

Several codes are available for modeling natural attenuation processes in groundwater. BIOPLUME II (Rifai et al. 1989) is a two-dimensional U.S. Environmental Protection Agency (EPA) code for handling oxygen-limited biodegradation. BIOSCREEN 3D (Newell et al. 1996) handles not only oxygen, but also biodegradation under the influences of other chemicals. BIOMOD 3-D (Draper Aden Environmental Modeling, Inc. 1996) couples to flow output from the U.S. Geological Survey flow model MODFLOW (McDonald and Harbaugh 1988) to simulate degradation of up to five species through first-order, oxygen-limited, anaerobic or Monod kinetics schemes, and sequential anaerobic or first-order biodegradation of daughter products. MT3D (Zheng 1992) and RT3D (Clement 1997) can also be used with a MODFLOW flow model to simulate contaminant transport and biodegradation. MT3D models sorption and can be used to characterize biodegradation in a simple fashion by using a first-order decay term. RT3D, which is an enhancement of MT3D, simulates multispecies reactive transport, including degradation with complex reaction kinetics.

For the current study, few biodegradation-related data are available for the confined aquifer. No clear upgradient/downgradient relationships are established for confined aquifer wells, and no concentration targets can be determined for calibration purposes. For these reasons, detailed biodegradation modeling was not a reasonable option for purposes of this study. MT3D was selected to model conservative degrees of sorption and simple first-order degradation along a conservative, hypothetical flow path to a well.

Section 4
Flow and Transport Modeling

4.1 Conceptual Flow Model

While the confined aquifer is believed to be a sandy deposit in a paleochannel, the extent and variable thickness of the aquifer are uncertain, as is the degree of hydraulic connection between the confined aquifer and permeable portions of the paleochannel walls. Although valuable data have been collected, any conceptual model of the confined aquifer will have a large degree of uncertainty because of the complex hydrogeological framework. The lack of a suitable conceptual model prohibited the construction of a detailed two- or three-dimensional flow and transport model.

A flowpath from the confined aquifer beneath J-Field to pumping wells in the region may not exist. However, to evaluate a worst-case hydrogeological situation, a simple, highly conservative flow model was designed. The modeling was simplified into a one-dimensional domain (Figure 4) representing flow conservatively assumed to travel directly from the confined aquifer beneath the TBP area to a hypothetical receptor well 8 km (5 mi) away. The hypothetical flowpath includes J-Field's confined aquifer (Pleistocene Talbot Formation) and permeable portions of the Cretaceous Patapsco Formation aquifer.

The direct flowpath assumption is especially conservative because (1) it ignores regional flow directions and actually could simulate flow in a direction opposite of the actual flow; (2) it ignores complex, three-dimensional flow paths that groundwater would have to follow while within the paleochannel, at the wall of the paleochannel, and within the permeable zones of the Cretaceous sediments; and (3) it ignores upward discharge to the bay.

4.2 Numerical Flow Model Setup and Results

Boundary conditions for this flowpath promote a fast rate of travel. A constant head value of 0.34 m (1.1 ft) MSL was assigned to the TBP area, in agreement with the mean water level of confined aquifer wells (Quinn et al. 1996). Pumping stresses are not modeled explicitly. At the downgradient end, a constant head value of –3 m (–10 ft) MSL was assigned to force a high hydraulic gradient across the modeling domain. The –3 m (–10 ft) MSL value is lower than that suggested in regional modeling of pumping stresses in the Patapsco aquifer (Fleck and Vroblesky 1996; Tenbus and Fleck 1996). Because of the model's boundary conditions, the calculated heads are independent of values for thickness and hydraulic conductivity. However, these values are required as input to the model, and the hydraulic conductivity value affects the flow rate. A confined aquifer thickness of 9 m (30 ft) was assigned on the basis of confined aquifer data
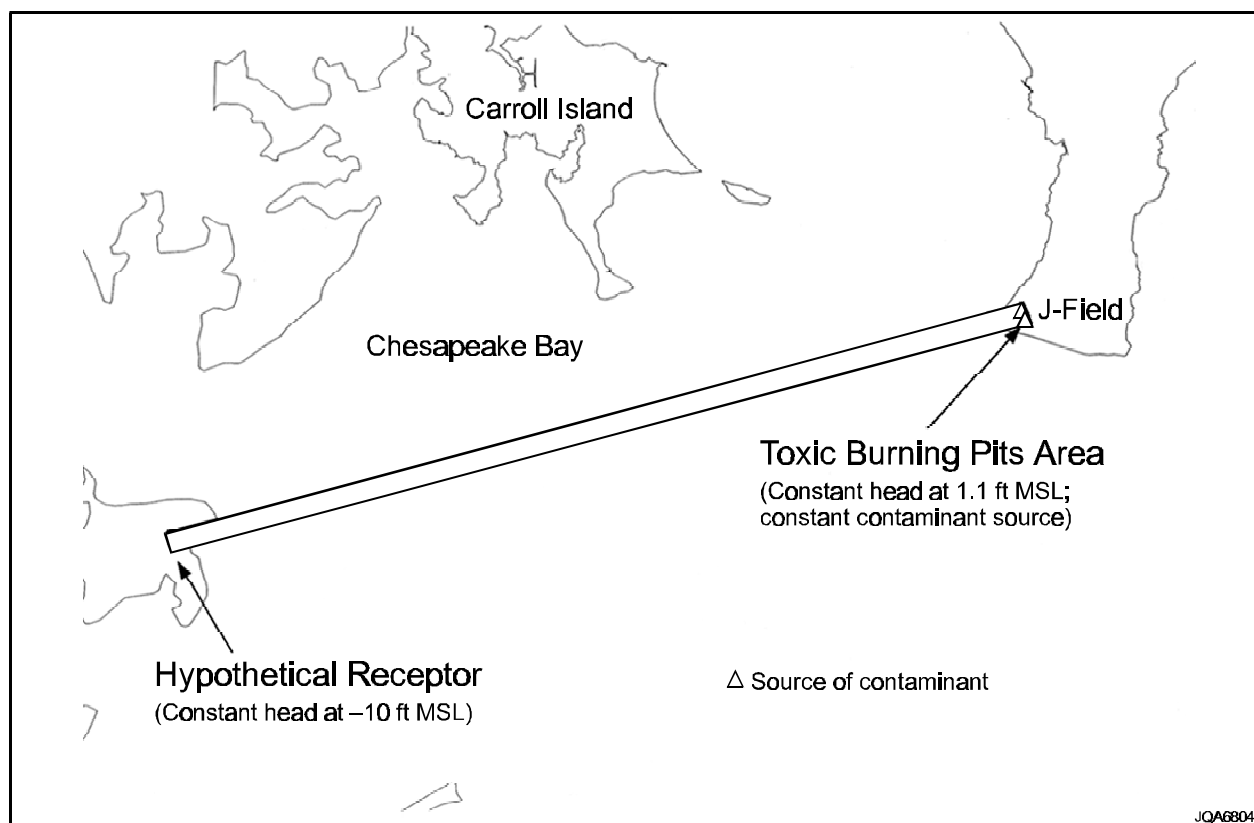
Figure 4 Domain of Flow and Transport Models

compiled by Hughes (1993). The hydraulic conductivity was set to the highest measured value at J-Field, a value of 274 m/d (900 ft/d) (Hughes 1993).

In area, the model grid covers 8,382 × 152 m (27,500 × 500 ft). The model was expanded from one row to two to facilitate contouring. In the direction of flow are 550 columns, each 15 m (50 ft) wide. The narrow width reduces numerical dispersion in the transport simulations.

Results of the flow model indicate linearly decreasing heads from the TBP area to the receptor well (Figure 5). This conservative flow field was used as input in the transport model.
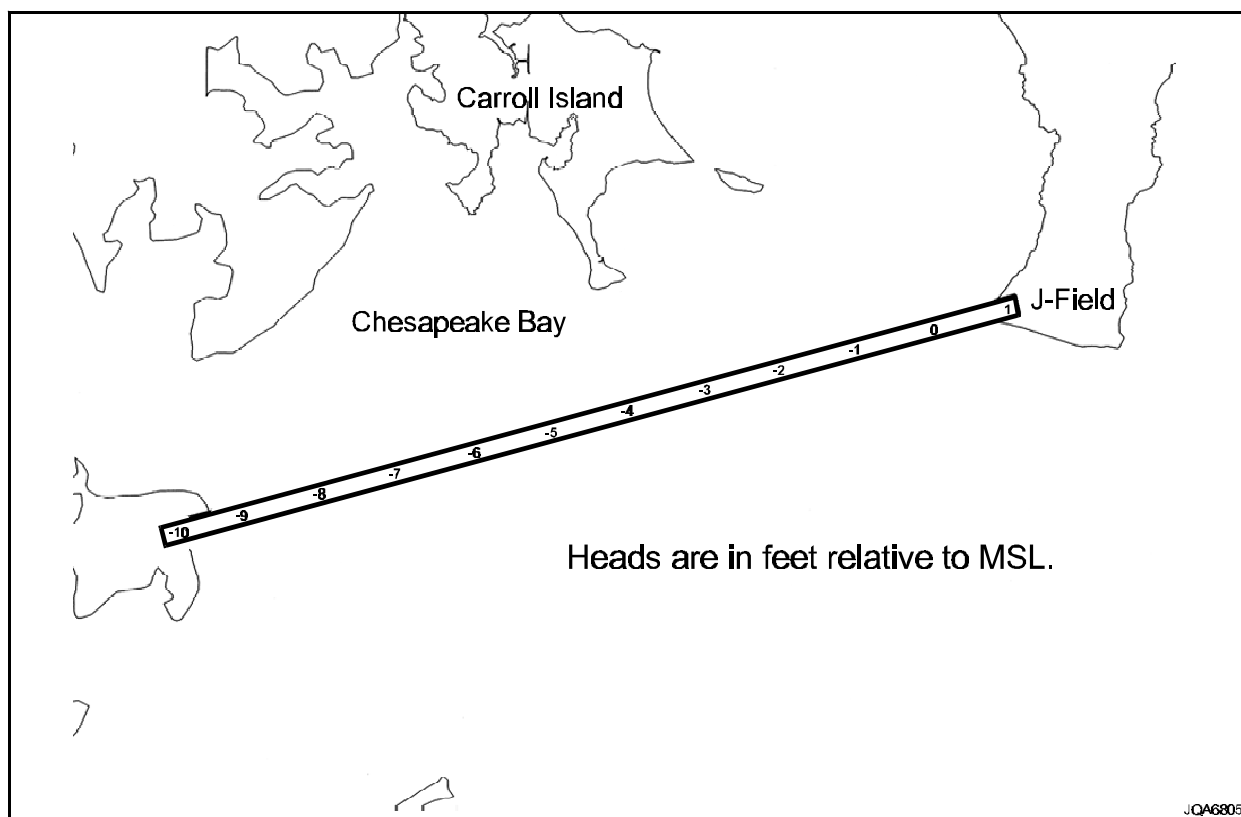
Figure 5 Heads of Flow Model

4.3 Conceptual Transport Model

TCE was selected as the primary contaminant of concern. This selection did not involve a detailed study of DNAPL migration from near-surface TBP sources downward through the confining unit, but rather an analysis of dissolved-phase TCE beginning in the confined aquifer. In addition to the direct flowpath assumption, other conservative assumptions included in the transport model were a high hydraulic gradient, high porosity, low attenuation, and no dilution along the flow path.

4.4 Initial Input Parameters

The MT3D simulations rely on the flow field generated by the MODFLOW flow model as the advective component of transport. For simplicity, dispersion was considered negligible. The effective porosity of the aquifer was assumed to be 0.3, and the bulk density was assumed to be 1,860 kg/m^3 (116 lb/ft^3). These values have not been measured but should be within 15% of actual values. They are, therefore, not considered to be major sources of error.

Because the confined aquifer is an anaerobic environment (Target Environmental Services, Inc. 1998), biodegradation of VOCs is assumed to occur along the hypothetical

flowpath. Drummond and Blomquist (1993) suggest the presence of anaerobic conditions in the deep aquifers of the region. Recent site-specific data indicate that the confined aquifer at J-Field is an anaerobic environment with natural attenuation processes likely degrading TCE to ethene and ethane (Target Environmental Services, Inc. 1998). In the model, TCE was assumed to biodegrade under these anaerobic conditions on the basis of the slowest half-life reported in the literature, 4.5 years (Howard et al. 1991; Cohen and Mercer 1993).

Sorption of TCE was assumed to occur following a linear sorption model. The lowest value of K_{oc} in the literature, 40 mL/g (Mackay et al. 1993), was combined with an f_{oc} of 0.001 in the range of values provided by Pankow and Cherry (1996). Although no site-specific f_{oc} data are available, Powars (1997) noted visible organic matter in the confined aquifer and in portions of the Cretaceous sands. The selected K_{oc} and f_{oc} values resulted in a K_d of 0.04 L^3/kg (6.4×10^{-4} ft^3/lb), or a retardation of 1.25, which is near the low end of literature values for TCE (Pankow and Cherry 1996).

Two conservative assumptions were made concerning the contaminant source in the model. First, the source assigned to the upgradient end of the model was conservatively given the concentration of 1,600 μg/L, the maximum measured value. Second, the source was specified as constant over time.

In addition to a base case using the above input values, several other scenarios were modeled to evaluate the sensitivity of selected input parameters. Each simulation covered 100 years; calculated concentrations were saved at 10-year intervals.

4.5 Results for Sorption and 4.5-Year Half-Life (Base Case)

The base case for analysis of the confined aquifer below the TBP included the conservative degrees of sorption and biodegradation, as discussed above. The results indicated that the zone of high contaminant levels does not extend as far as the hypothetical receptor (Figures 6 to 11). As a result of the first-order decay, the 5-ppb contour stabilized 3.2 km (2 mi) from the receptor in less than 50 years. Even the 1-ppb contour stabilized in less than 70 years. Despite the small cell size, the results were affected by a low degree of numerical dispersion (discussed below), which would extend the plume, in keeping with the conservative design of this study.

4.6 Results for Sorption Only

This scenario was analyzed primarily to determine the effect of numerical dispersion on results. Because no decay or hydraulic dispersion was modeled, the theoretical results should represent a sharp concentration front. Modeled results showed a reasonably low degree of numerical dispersion because the concentration front was fairly narrow.
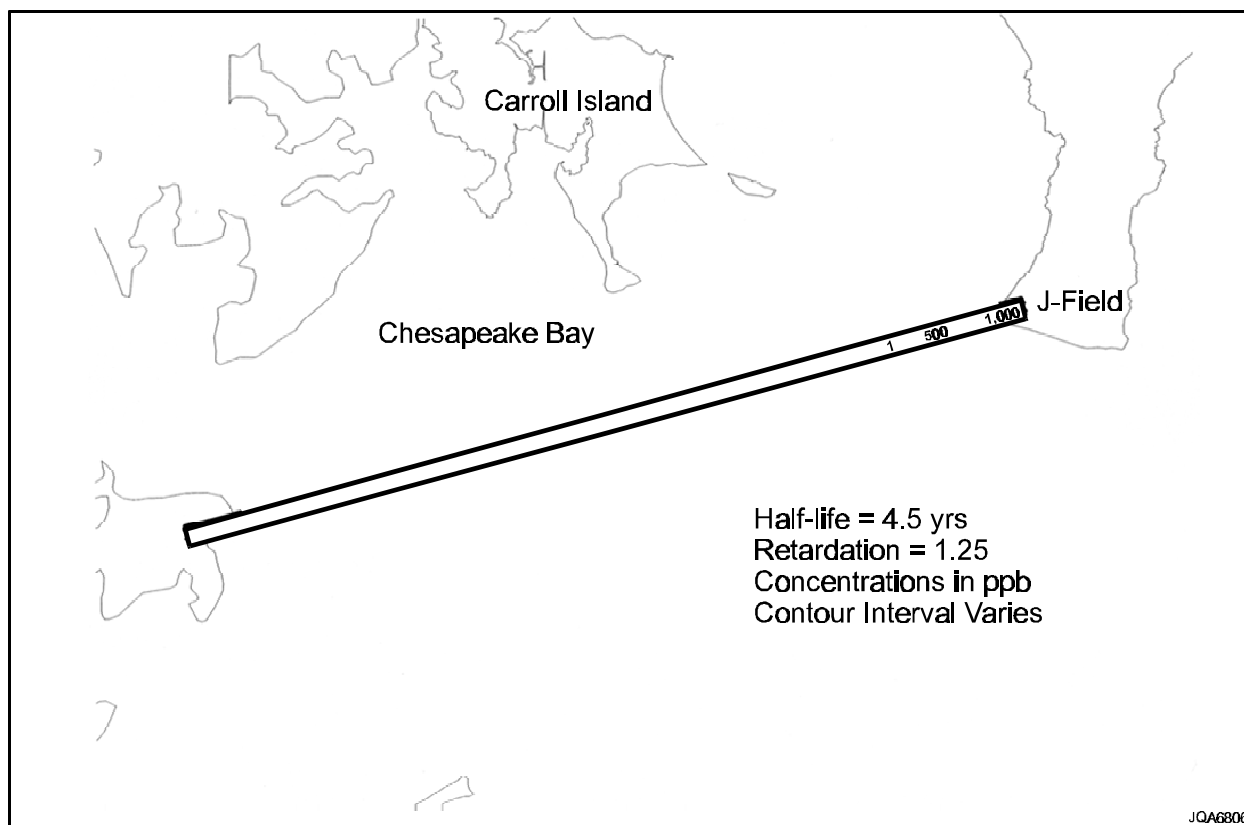
Figure 6 Base Case Transport Results for Simulated TCE Concentrations after 10 Years of Simulation

4.7 Results for 4.5-Year Half-Life with No Sorption

Because R is 1.25 in the base case, the results for this scenario simply showed the plume traveling 25% faster and extending 25% farther with no retardation ($K_d = 0$; therefore, $R = 1$).

4.8 Results for Sorption and Doubled Half-Life

With a half-life of 9 years (double the highest value in the literature), the decay rate was half that of the base case. The results for this scenario showed the 1- through 10-ppb contours reaching the receptor after approximately 75 years. The bulk of the plume, however, should stabilize in 60 years; the 50-ppb contour should be over 1.6 km (1 mi) from the receptor.
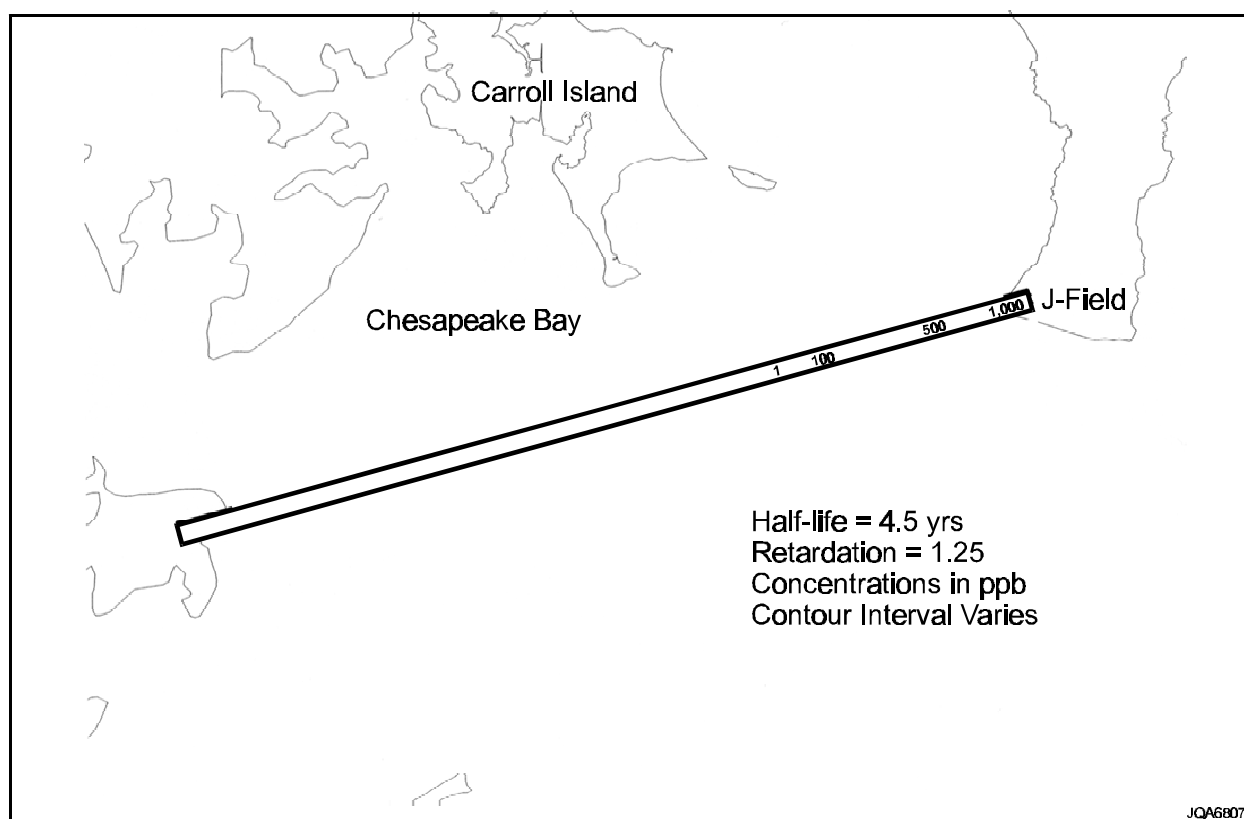
Figure 7 Base Case Transport Results for Simulated TCE Concentrations after 20 Years of Simulation
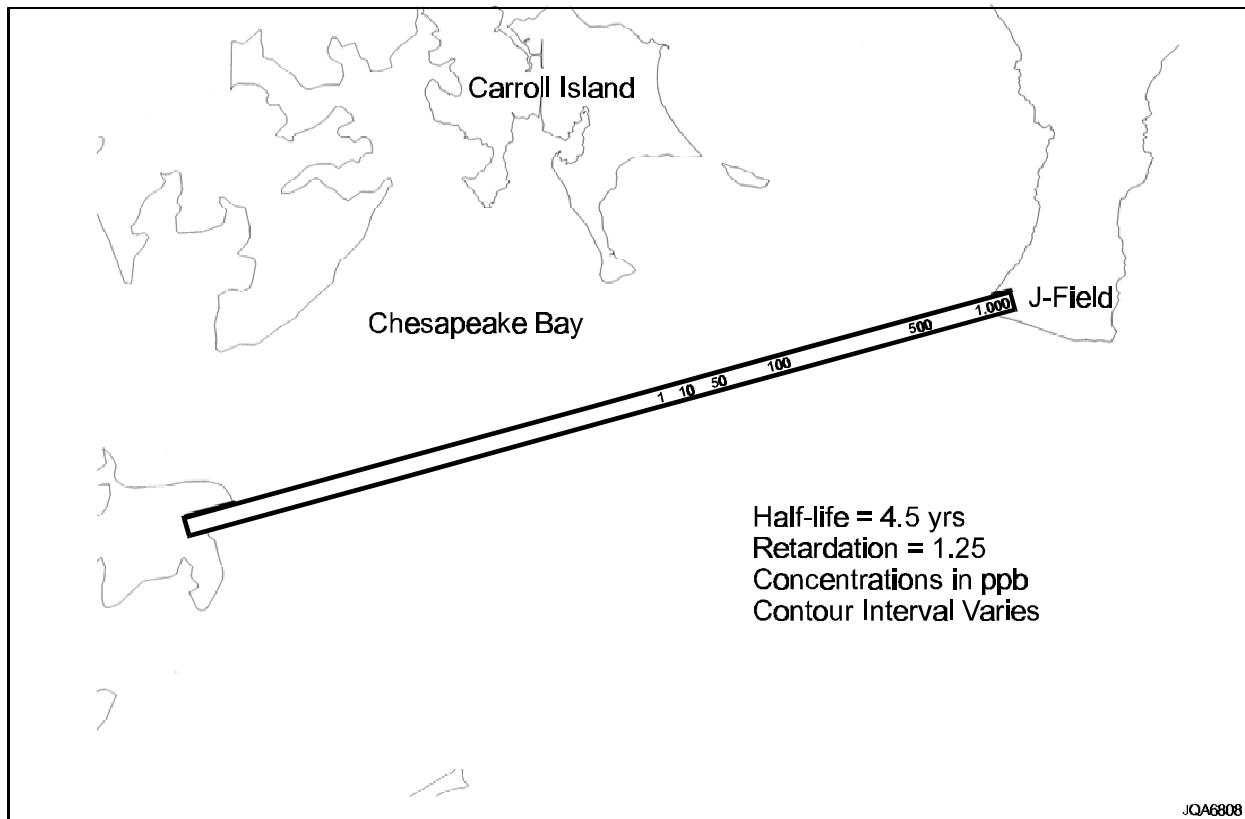
Figure 8 Base Case Transport Results for Simulated TCE Concentrations after 30 Years of Simulation

Figure 9 Base Case Transport Results for Simulated TCE Concentrations after 40 Years of Simulation

Half-life = 4.5 yrs
Retardation = 1.25
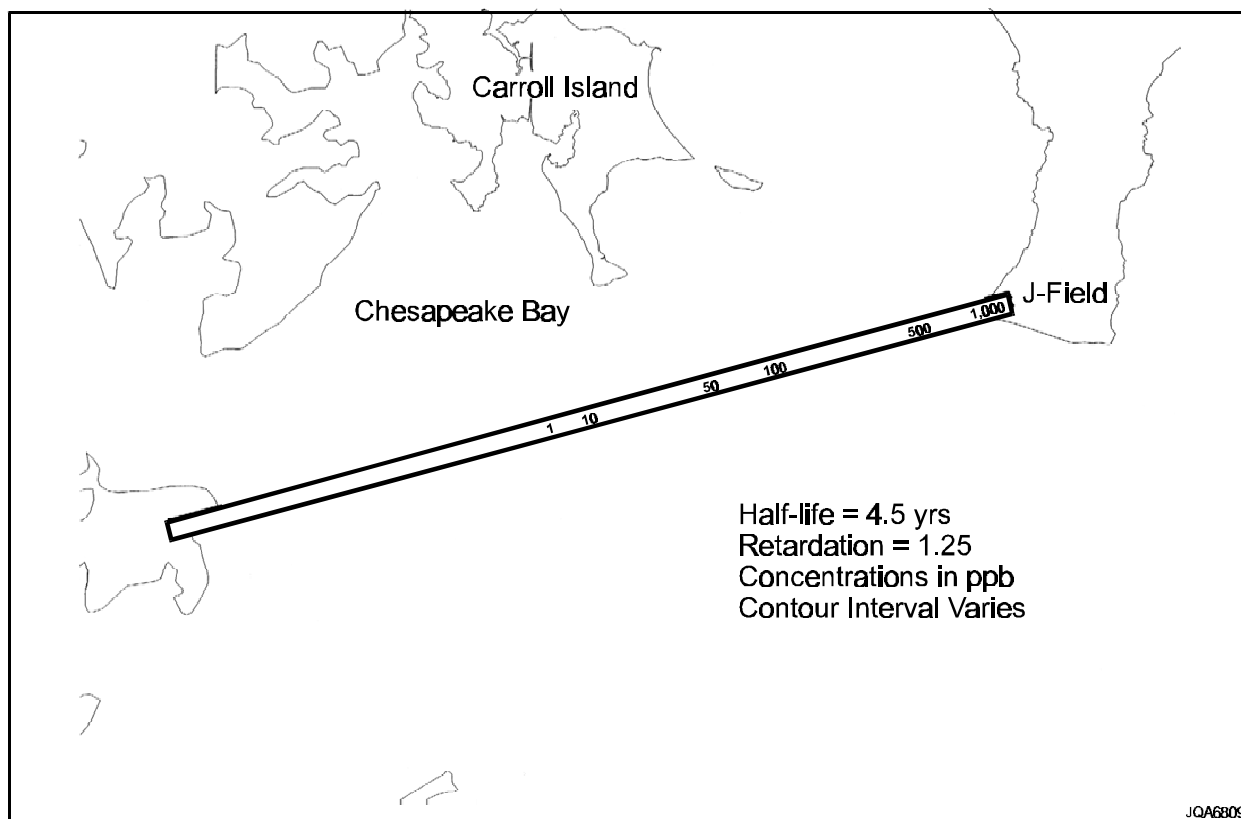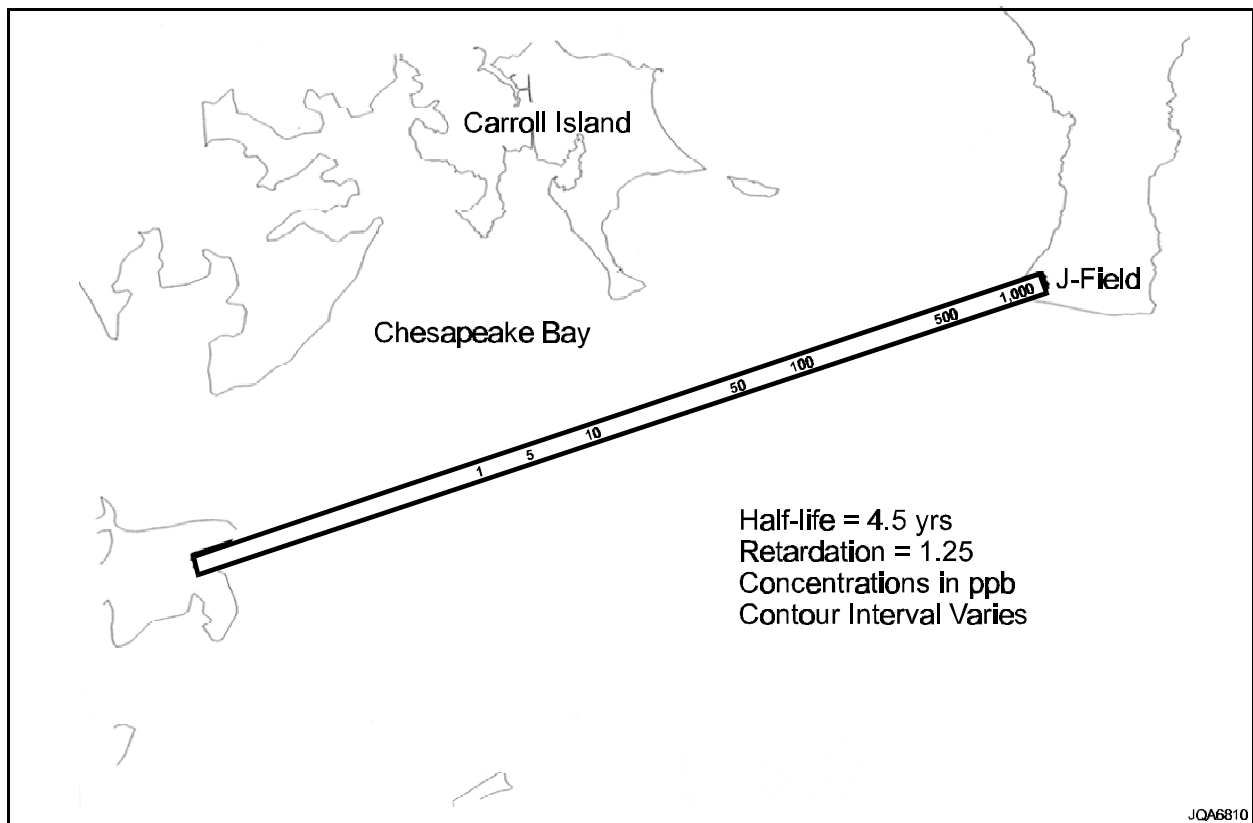Concentrations in ppb
Contour Interval Varies

Figure 10 Base Case Transport Results for Simulated TCE Concentrations after 50 Years of Simulation
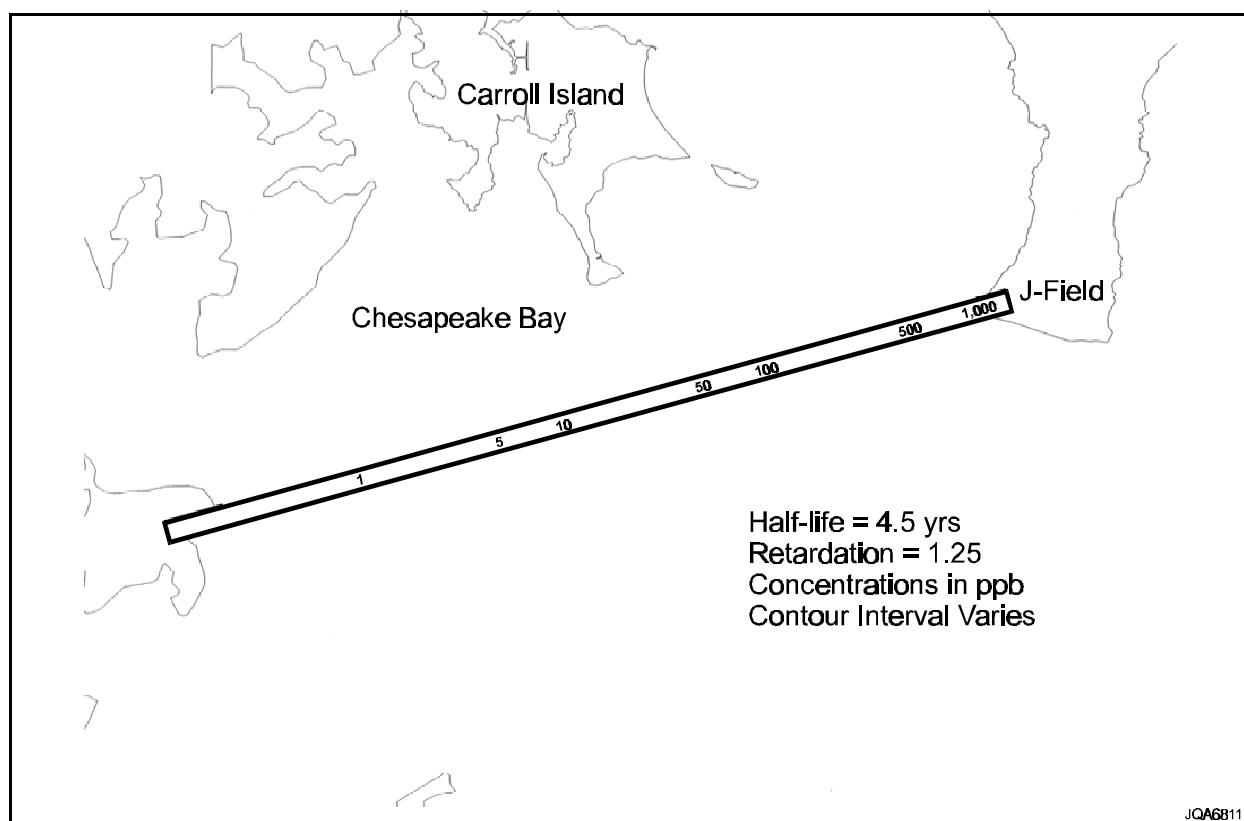
Figure 11 Base Case Transport Results for Simulated TCE Concentrations after Reaching Steady State at 60 Years of Simulation

Section 5
Discussion of Results

A one-dimensional transport model with a continuous source, sorption, and first-order decay can be expected to reach a steady state; the contaminant concentrations should decrease from the source value to essentially zero downgradient. The parameter-dependent questions are

- How much time is needed before steady state is achieved?

- What is the distribution of concentrations once the plume has stagnated?

The results of this study indicate that the distance from the source to the hypothetical receptor is sufficient to overcome the relatively slow rate of biodegradation and low degree of sorption. In the base case, the 5-ppb contour is at steady state after less than 50 years of simulation.

The assumed first-order biodegradation rate equal to the slowest rate reported in the literature was sufficient to attenuate the plume before it could reach a receptor. The sensitivity of this parameter was apparent; when the rate was halved, significant concentrations reached the receptor. However, the likelihood of these concentrations actually reaching the receptor is negligible, because of the model's other simplifying assumptions.

Concentrations at any distant pumping well that could be affected by groundwater contamination beneath J-Field would be significantly lower than those predicted by this simplified one-dimensional model, because a pumping well would be drawing in clean water from other directions. This dilution effect was not considered in the simulations.

MT3D calculated a mass balance for each time step of each simulation. Each computer run in this study had a mass balance well below 1%, which signifies that mass was conserved and that the results, from a computational standpoint, are accurate.

In this analysis, the degradation products were ignored. Although TCE degrades to VC, which is highly toxic, VC also degrades to ethene/ethane. This preliminary modeling evaluation focused on whether TCE has a strong likelihood of reaching a receptor. Future work could address similar worst-case modeling of TCE and its degradation products (DCE, VC, ethene, ethane).

Section 6
Conclusions

The results from highly conservative modeling indicated that groundwater contamination would have no impact on the nearest receptor. The model can therefore be a useful tool in proposing either a no action or a natural attenuation alternative for the confined aquifer, especially if source removal or other remedial actions are performed in the near-surface of the TBP area of J-Field.

The degradation rate in the confined aquifer beneath J-Field and along any possible pathway has not been measured. The decay rate may not follow a first-order model, and site-specific factors such as redox conditions will have a major influence on natural attenuation processes. However, complete biodegradation of TCE to ethene and ethane is believed to occur in the confined aquifer beneath J-Field on the basis of recent field sampling of natural attenuation indicators (Target Environmental Services, Inc. 1998).

Modeling included an extremely conservative direct flowpath to a hypothetical receptor, together with other conservative assumptions regarding the source strength, the sorptive capacity of aquifer materials, and flow rate. Mixing of groundwaters at the downgradient pumping well was ignored, as was the possibility of upward discharge to Chesapeake Bay. These assumptions may diminish the uncertainty in the rate of biodegradation of contaminants emanating from J-Field.

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